PREPARATION OF ZINC NITRIDE

BY

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ARMOUR INSTITUTE OF TECHNOLOGY

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THE PREPARATION OF ZINC NITRIDE AND ITS ALLOY WITH ZINC

A THESIS

PRESENTED BY

WALTER J. BENTLEY AND PAUL L. STERN

TO THE

PRESIDENT AND FACULTY

OF

ARMOUR INSTITUTE OF TECHNOLOGY

FOR THE DEGREE OF

BACHELOR OF SCIENCE

IN

CHEMICAL ENGINEERING

MAY 27, 1920

APPROVED: H. McCormack

Professor of Chemical Engineering

Dean of Engineering Studies

Dean of Cultural Studies

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PREFACE

While realizing that we have but barely touched on the many phases of the problem, we have set forth and that much hard and exacting work yet remains unaccomplished, we present this thesis to the President and Faculty of the Armour Institute of Technology.

It is to be hoped that at some future time we ourselves or others may have the opportunity of carrying the work forward. We have broken the ground. It remains for others to uncover the true value of the work which gives such promise of success.

We wish to express our thanks to Prof. McCormack for his many suggestions and his able direction of our work. Prof. Tibbals and Prof. Freud are also to be thanked for their assistance.

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Walter J. Bentley
Paul L. Stern

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STATEMENT OF THESIS PROBLEM

Taking into consideration the large tonnage of zinc available in this country, it is suprizing that it has found so few industrial applications. Its chief uses as a metal are in the manufacture of galvanized iron, as a roofing material, and as a component of various alloys as brass, bronze and gun-metal.

This thesis was undertaken with a view of finding a new series of alloys. It was thought that a new constituent introduced into the zinc in amount perhaps not over 2% would change its physical properties to a marked degree. It was decided that this would best be nitrogen present in the zinc as zinc nitride. The work then resolved itself into the determination of the best conditions for the preparation of zinc nitride and its alloy with zinc.

The presence of ferric carbide in iron

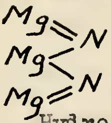
has given us the valuable series of steels. Many claim that the whole function of the carbide consists in by its mere presence retarding or preventing the formation of large crystals of iron. The large crystal structure of zinc results in a brittleness and lack of mechanical strength. On this account zinc cannot be machined and, notwithstanding its many valuable properties, loses most of its commercial value. It is expected that the presence of zinc nitride will do for zinc what ferric carbide does for iron.

THE NITRIDES OF THE METALS

THEORY OF NITRIDE PREPARATION

Nitrides and Trinitrides

It is unfortunate that under our present system of chemical nomenclature we have no set means of differentiating between the two great classes of nitrides. There are the salts analagous to magnesium nitride- Mg_3N_2 - and also those analogous to what we can best call perhaps magnesium tri-nitride - MgN_6. The structural formulas of the two are generally accepted as:-



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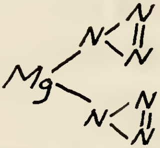


Hydro nitric acid has at various times been known as (25)[i] azo-imide, hydrozoic acid, triazoic acid, hydro nitrous acid, hydrogen nitride and nitrogen hydride. Its salts have gone under names derived from each of the above acid names. It has been suggested that the ring of three nitrogen atoms be called the nitrine group and the hypothetical

---

[i] Numbers refer to Bibliography.

compound $(N_3)_2$ - analagous to Cl_2, Br_2 and I_2 - be called nitrine. Probably the best solution of the difficulty is to call HN_3 hydronitric acid and call its salts tri-nitrides as MgN_6, magnesium tri nitride.

It is very probable that many of the early investigators on the subject obtained a tri nitride while working for a nitride and thus much of the confusing and conflicting data can be explained. In the instance of the Frankland work (1) on zinc amide this is evidently the case. In common with many others he describes Zn_3N_2 as a highly explosive powder decomposed by water, alcohol and moist air, and these properties are not sustained by the more recent work. We are concerned only with the nitrides of the metal in this thesis and the tri nitrides will be dropped from the discussion.

The Activity of Nitrogen

It is incorrect to speak of active and inactive elements. Nearly all the elements have both weak and strong affinities. Sometimes, however, their strong affinities are for the common or better known elements and we say that the element is active. If on the other hand its strong affinities are for the less common elements we say the element is inactive.

Nitrogen is unfortunate in belonging to the latter class. Its affinities are masked by the facts that:-

1.) The elements for which it shows its strongest affinities are those whose powers of self combination are most strongly developed or whose power of combination with oxygen is marked.

2.) Nitrogen itself has the power of self combination strongly developed. Ex: N_2 in gaseous nitrogen and the diazo group $- N = N$.

3.) The elements for which it exhibits its strongest affinities are somewhat uncommon; nitrogen expends its energies mainly on the intermediate groups of the Periodic System - Groups 3, 4 and 5,-and but little for others such as the alkali and halogen elements. The B, Si and P compounds with N are remarkable for their stability. P_3N_2 must be heated in oxygen to a temperature at which hard glass melts before the oxygen acts on it notwithstanding the great affinity of P for O.

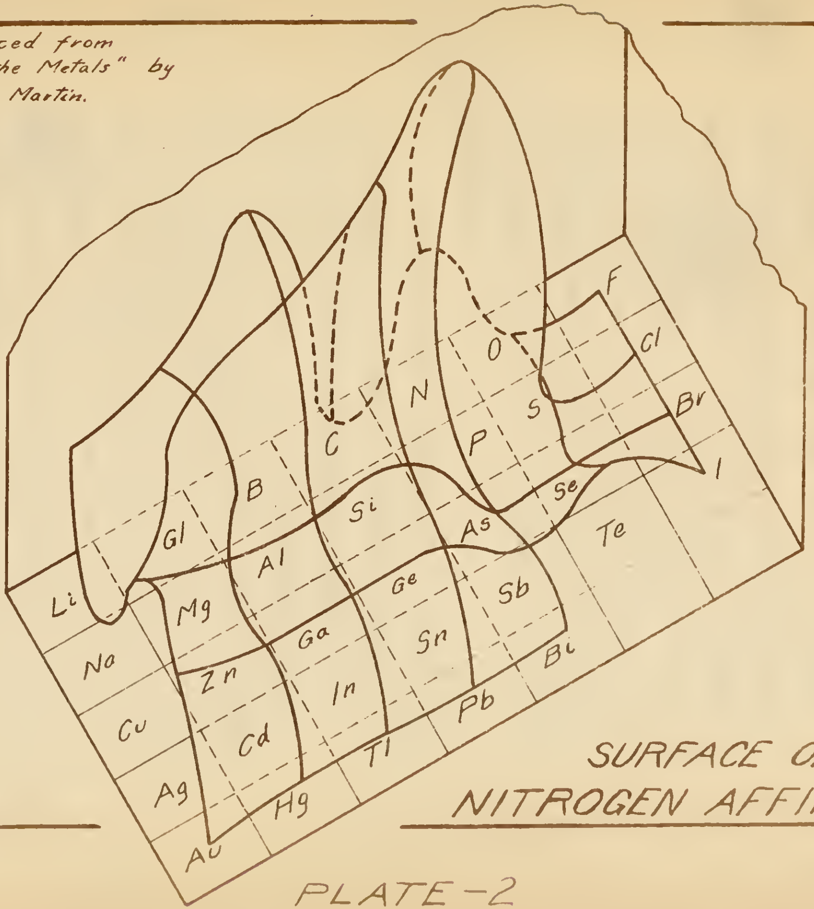
Geoffery Martin (26) has developed this viewpoint very well and drawn a surface representing the affinity of nitrogen. He divides a plane into squares each representing an element placed with regard to the others so as to agree with the Periodic System. On this he develops a surface the height of which above the plane is an indication of the chemical affinity of nitrogen for that element.

Relative Chemical Affinities of N.

Li – 4.1	Gl – 5.0	B – 8.0	C – 0.5	N – 4.0	O – 0.2	F – 0.1
Na – 1.0	Mg – 6.0	Al – 7.0	Si – 9.0	P – 11.0	S – 0.2	Cl – 0.1
Cu – 0.4	Zn – 3.0	Ga – 3.0	Ge – 3.0	As – 0.2	Se – 0.2	Br – 0.1
Ag – 3.0	Cd – 2.5	In – 2.5	Sn – 2.5	Sb – 1.0	Te – 2.0	I – 0.15
Au – 0.1	Hg – 0.2	Tl – 0.2	Pb – 0.2	Bi – 0.2		

PLATE – I.

Reproduced from
"Affinities of the Metals" by
Geoffery Martin.



SURFACE OF
NITROGEN AFFINITIES.

PLATE – 2

Formation and Decomposition of Nitrides

Geoffery Martin (loc. cit.) has shown that nitrogen can have very strong affinities for some elements. Added to this, the fact that N will combine rapidly (14) with the alkaline earths (for which its affinity is supposedly small) in the complete absence of C , argues considerable chemical affinity for nitrogen.

In many cases, however, the temperature of decomposition and of formation are so close together (or even overlapping) that very little nitrogen is fixed permanently as nitride. However, even in these cases, the metal is profoundly changed in its physical properties. When the altered metal is examined under the microscope (5) it is seen that the nitride must be more fusible than the metal for a characteristic spongy structure due to the escape of innumerable minute bubbles of the gas is clearly visible.

White and Kirschhamn (6) lay the fault of poor yields of nitride to the formation of a condition of equilibrium between the metal, the ammonia and the H from the dissociated ammonia.

Beilby and Henderson (5) claim that, at the temperature of formation, the per cent of dissociation of the ammonia reaches a stage where a sufficient excess of ammonia is no longer present. As the formation of nitride proceeds inward from the surface of the metal a point is reached where the hydrogen is in excess of the ammonia and a balance being established no further nitride is formed. The N and H escaping give the metal its characteristic porous structure.

It is quite possible also that we have to deal with surface action of the ammonia and that the problem is partly one of exposing a new fresh surface to the gases.

Zhnkov (13 and 27) claims from a study

of the dissociation pressure and electrical conductivity of the compounds of Mn, Cr and Ti with N that in these cases nitrides are not formed but that the N is present only as a component of a solid solution of N and the metal.

The maximum absorbtion of N is determined by:-

1.) The state of aggregation of the metal,
2.) Extent of surface exposed,
3.) Temperature,
4.) Excess of reacting gas,
5.) Time.

It had been hoped from the close proximity of zinc to Mg in the Periodic System and the ease of preparation of Mg_3N_2 that zinc nitride could be prepared without difficulty. This, however, is not the case. The Temperature of formation of zinc nitride is slightly lower than that of magnesium nitride, but all other conditions seem equal. It is

the authors' opinion that the reason lies in the greater ease with which magnesium may be kept unoxidized in a fine state of subdivision than in the case of zinc.

THE PROPERTIES OF THE NITRIDES

Occurence

All the metals with the exception of Au, Ni, Co and Pt (17) seem to form nitrides by some reaction. As far as the authors are aware, no nitrides are found in nature.

Matignane (9) conducted an investigation to find the amount of zinc nitride present in commercial zinc. He states that the commercial zinc, other than powder, does not always contain nitrogen and never more than .003 to .004%. Zinc dust contains a higher percentage of nitride but, under the best conditions for its formation, it never exceeds .42%. Zinc oxide contains no nitride.

Thurston (28) found that commercial iron and steel often contain N, probably as iron nitride, up to .1%, but other men (11) have found much higher percentages.

Appearance

The literature on the subject of the nitrides, especially as regards their color and physical properties, is very unreliable. It is probable that many investigators mistake the tri-nitrides for nitrides and in some cases may not have a pure product but one with considerable admixture of the original metal or oxide. Thus the color of zinc nitride is given by various authorities as green, gray, brown, black and yellow. From our own work we are inclined to say that a pure sample of zinc nitride would be black or very dark gray.

Boron nitride is said to be white; aluminium nitride, white or yellow; ferric nitride, black; ferrous nitride, black; calcium nitride, brown; chromic nitride, dark gray; columbium nitride, black; magnesium nitride, greenish yellow; mercuric nitride, brown; potassium nitride, dark gray; selenium nitride,

yellow; sodium nitride, dark gray; and tantalum nitride, yellow.

Compounds derived by the replacement of H in ammonia by the lighter metals are entirely non-metallic (29). The nitrides of the heavy metals of groups 6, 7 and 8 are generally metallic. Those positively described as metallic are Mn_3N_2, Mn_5N_2, Mn_7N_2, CrN, Mg_3N_2, Fe_5N_2, Fe_2N and FeN.

Stability

There is quite a little variance of opinion as regards stability. Warren (23) says that all the nitrides are characterized by great instability toward heat. Fischer and Schroeter (17) claim that all the nitrides of metals of high molecular weight as Cd, Hg, Pb, and Bi are explosive and that the others decompose quietly on careful heating. To quote from their work. "With the exception of the first group, where exceptions occur, the A sub-group of each group of the Periodic System

contains only metals forming nitrides stable at room temperature. The B sub-group contains only metals forming nitrides unstable at room temperatures and decomposed by shock or heating." Andrews (11) has shown that iron nitride was stable after several weeks heating at red heat in a vacuum.

It has been claimed by various workers (19, 30 and 21) that the nitrides of Zn, Al, Mg, Fe, Cu, Mg, La and Cr are decomposed by water to yield the hydroxide and ammonia. However true this may be, the authors were unable to find any action between zinc nitride and water.

The nitrides in general are not fused or decomposed except at very high temperatures when out of contact with the air. However they show a great tendency to oxidize with the evolution of nitrogen even at moderately elevated temperatures.

General Properties

Nitrides are in general very hard and brittle and crumble to a powder easily (23).

Nitrides of Li, Cr and Mn have been considered by some to be solid solutions of N in the metal (12) and are highly magnetic. Manganese nitride is fully the equal of iron in this respect.

The electrical conductivity of magnesium nitride was determined by Zhnkov (27) to be 2.1×10^6 which is very high considering that copper has a specific conductivity of only 6.3×10^5.

Andrews (11) found that nitrogen in small quantities in iron and steel depressed and widened the critical ranges and in large amounts suppressed them entirely. Thus .3% N entirely suppressed the critical ranges and .25% N in a .6% carbon steel lowered Ar to a marked degree. The steel could be de-nitrogenized only by several

weeks heating in a vacuum.

Guntz (32) heated 1 g. lithium nitride and 10 g. ferrous potassium chloride and obtained a violent reaction. After washing in an atmosphere of CO_2, pure ferrous nitride, Fe_3N_2, was obtained as a black easily oxidizable powder. Lithium nitride heated with ferric potassium chloride or chromic chloride gave ferric nitride, FeN, or chromic nitride, CrN.

Eidmann (31) heated SiN with an excess of Mg powder and obtained Mg_3N_2 and a residue of Mg and MgSi. With Ba_3N_2 the results were analogous. Walk (15) showed that Fe would not react with barium nitride to give Fe_2N.

Fowler (33) has made a remarkably complete study of iron nitride and assigns the formula Fe_4N_2 rather than Fe_2N. The properties he ascribes to it are:-

It is oxidized at 200° when heated in an atmosphere of oxygen,

It evolves N and burns in an atmosphere of Cl to ferrous chloride on slight heating but gives no reaction with Br or I.

Mineral acids convert it to ferrous and ammonium salts and liberate H.

Heating in H_2S to about 200°C gives the reaction

$$2 Fe_2N + 6H_2S \rightarrow 4FeS + 2NH_4HS + H_2$$

Heating with phenol at 220° gives no reaction.

Heating with C gives no reaction.

Heating with C and Na gives Prussian Blue.

Steam gives a very slight but continuous evolution of ammonia.

Its temperature of decomposition is above 600°C.

LABORATORY PREPARATION

The experimental work on the nitrides is in a very disorganized stage. Much work has been done on the subject but the methods seem so widely divergent and immature at present that little comparison is possible. Much of the work has been reported in the Russian and German periodicals and is very vague in detail. With the exception of the classical experiments on magnesium nitride and the very recent work on aluminium nitride, the work is fragmentary and scattered over the last 140 years - indeed much of it was performed in the early part of the 19th century. The greater part of the material on magnesium and aluminium nitrides has been ommitted in the interests of the data on the lesser known nitrides.

In preparing the following account of nitride preparation, we have endeavored to follow as far as possible the preparation of

nitrides in general while stressing their applicability to the case of zinc. The work may probably be best classed under six general heads and it will be so considered. Nitrides are prepared by:

1) Decomposition of an amide
2) Direct combination between the metal and a gas
3) Replacement of a hydride
4) Partial oxidation of an organic body
5) Reduction of the oxide
6) Electrolysis.

1) Decomposition of an Amide

Probably the first man to prepare zinc nitride and certainly the most often quoted is Frankland (1). There is, however, some doubt of its value in view of the properties he ascribes to it and in comparison with more recent work. It is very likely that what he

obtained was not the zinc nitride we are considering but the salt of hydro-nitric acid. His method with zinc taken as an example is as follows:-

Dry ammonia gas is passed through an ethereal solution of zinc ethyl and copious fumes of ethane are evolved. After about an hour the absorbtion ceases and we get a voluminous precipitate of zinc amide. This is white, amorphous and decomposed by both water and alcohol.

$$Zn(C_2H_5)_2 + 2NH_3 \rightarrow Zn(NH_2)_2 + 2C_2H_6$$

If this zinc amide is heated to a dull red heat (about 200°C) we get a gray pulverulent substance which probably corresponds to the formula for zinc nitride.

$$3Zn(NH_2)_2 \rightarrow Zn_3N_2 + 4NH_3$$

This is neither fused, decomposed nor volatilized at a red heat when out of contact with the air.

2) Direct Nitrification with Gases

1a) With Ammonia The preparation with ammonia gas seems to have attracted the most attention and to promise the best results. It certainly seems to be the best adapted for commercial preparation of most of the nitrides - especially those whose temperature of formation is below 850° C.

Probably the first work was done by Berthollet and Therard (2), who noted that an iron wire exposed to ammonia at a red heat did not increase in weight but became very brittle. Savard (3) observed that after ammonia was passed over hot iron, the metal became softer and then after the second hour heating became hard and behaved like steel. These investigators did not recognize the formation of iron nitride.

Despnetz (4) obtained iron nitride by heating iron in a current of ammonia and found the nitrogen content varied from 7% up to 11.5%, the theoretical amount. He reported

iron nitride as a white brittle material.

Beilby and Henderson (5) noted that most metals were profoundly altered in almost every characteristic by exposure to ammonia at elevated temperatures. They attributed this more to alternate formation and decomposition of the nitride rather than to a permanent deposit of nitride.

White and Kirschbaum (6) experimented with passing dried ammonia gas over zinc at a red heat. From their experiments they concluded that the zinc nitride begins to decompose slightly below 600° C (at which temperature about 6% is destroyed by heating for one hour) and that complete conversion is impossible. With sheet zinc only a trace of nitride could be obtained and with granulated zinc but 2% conversion was possible. In a test run where the ammonia was bubbled through molten zinc, a sample obtained from the spattering thrown up on the side walls was analyzed and gave 3.1%

nitrogen. A run made with zinc dust gave 10.6% nitrogen and 86.83% zinc.

The nitride ranged from a brown in the lower yields to a black powder in the higher yields. They found that the two could be separated with alcohol - the brown being suspended and poured off. The black powder was washed with ether and dried in vacuo and on opening the desicator the odor of ammonia was apparent and the % nitrogen had not increased. It was remarked that though the temperature was 200° C above the melting point the zinc held its form and did not melt.

Henderson and Galletly (7) obtained substantially the same results but lay the fault of the low yields more to the reducing action of H from dissociated ammonia rather than to a reversal of the reaction due to temperature. They fixed the initial decomposition point of ammonia at 200° C.

Fremy (8) obtained iron nitride by heating anhydrous ferrous chloride in a stream of dry ammonia. His product contained

9.3% N while the formula Fe_2N requires 11.5%.

b) With Nitrogen These experiments where the metal was exposed to the action of nitrogen seemed to give rather meager results but those where an amalgam was used were quite successful. It is quite probable that the amalgam would work just as well or better in an atmosphere of ammonia.

Matignore (15) confirmed the work of Bniegleb and Genter on heating zinc filings in a furnace to a faint red in a current of nitrogen to obtain zinc nitride. However he was only able to prepare a sample having .42% zinc nitride under the best conditions. He also found that a fused mixture zinc and zinc nitride in exposure to a current of N lost a portion of its nitrogen.

Andrews (11) was able to obtain as high as .3% nitrogen in a .6% carbon steel by melt-

ing the steel under a high pressure of nitrogen.

Zhukov (12 and 13) found Mg and Ca absorbed N when heated in it above 780° C; Al and Cr above 800° C; Mn above 850° C and Ti above 900° C.

With Amalgams 15-20% amalgams of Ba, Sr and Ca prepared (14) by electrolyzing a solution of the chlorides with a Hg cathode and in the case of Ca concentrating by distillation. When these were heated in dry N at a dull red heat for a half hour till the Hg was expelled and then to a bright red heat for a few minutes, the nitrides of the metals were obtained. In general they were brown semi-metallic products.

Wolk (15) prepared a 10% Ba amalgam and heated it in an iron boat in an atmosphere of N while the temperature was gradually raised to 1000° C. He obtained a product of Ba_3N_2 containing considerable iron and was able to increase the iron content by adding Fe filings. He concluded that the iron simply alloyed and that iron nitride was not formed by inter

ing the steel under a high pressure of nitrogen.

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action with the Ba_3N_2.

c) With Cyanogen Glucinum nitride has been prepared by passing $(CN)_2$ over metallic beryllium at 800° C.

2) In the Electric Arc

Fisher and Schroter (17) has prepared nitrides of many metals in an arc between a silver anode and a cathode of the metal whose nitride is required. The electrodes must be immersed in a solution of approximately 90% liquid argon and 10% liquid N. The nitride is formed by inter action between the metallic vapors of the arc and the nitrogen and is cooled by the liquid gases. The product is never pure being contaminated and colored black by unconverted metal. The following metals were converted to nitrides: Na, K,

Rb, Cd, Hg, In, Tl, Sr, Pb, As, Sb, Bi, Se, Te, and Mn.

3) Replacement of a Hydride

The nitrides of Cr, Cd and Ca have been prepared (18) by heating the hydride in an atmosphere of nitrogen at from 600-700° C. A small amount of nitrogen is also absorbed by the hydrides at room temperature - most probably by occlusion. An alloy, or SrH_2 and CdH_2 under the same conditions, gives a better replacement.

This alloy of SrH_2 and CdH_2 can be made by heating an alloy of Sr and Cd in a closed space with H. The hydrogen is absorbed at 340° C, evolved again at 470-570° C and again absorbed at a slightly higher temperature.

4) Partial Oxidation of Organic Bodies

1) Carbides. Vaurnos (16) claims that carbide when heated in the presence of ammonium nitrate and nitrogen gives the nitride. Ex: Calcium nitride has been prepared in this way.

$$3CaC_2+12NH_4NO_3 \rightarrow Ca_3N_2+6CO_2+11N_2+24H_2O$$

Rossel (19) has perfected a method by which a metal is converted to the nitride by heating with a carbide- preferably calcium carbide. The metal powder is mixed with finely ground calcium carbide and heated to a dull red in a crusible exposed to the air or in a tube through which air is passed.

$$CaC_2+3Zn+2N+5O \rightarrow CaO+Zn_3N_2+2CO_2$$

The nitrides of Cu, Mg, Zn, Al and Fe have been prepared by this method.

2) Cyanamide Barium cyanamide (16) in the presence of N with ammonium nitrate gives the barium nitride.

$$3BaN_2C + 6NH_4NO_3 \longrightarrow Ba_3N_2 + 3CO_2 + 8N_2 + 12H_2O$$

3) Cyanide

a) The cyanide of the metal (16) heated with ammonium nitrate in the presence of N gives the nitride.

$$3Zn(CN)_2 + 12NH_4NO_3 \rightarrow Zn_3N_2 + 6CO_2 + 14N_2 + 24H_2O$$

b) Vournas (20 and 21) has shown that Al as an impalpable powder reduces many organic N compounds. Thus the carbomide:

$$CS(NH_2)_2 + 4Al \rightarrow 4AlN + H_2S + H_2 + C$$

Potassium or ammonium thiocyanates if dried and mixed with Al powder react if heated in a covered crucible,

$$2KCNS + 2Al \rightarrow K_2S + 2AlN + 2C$$

but the reaction also tends to reverse and give us the sulfide.

$$2K_2S_2 + 2AlN + 2C \rightarrow Al_2S_3 + 2KCN + K_2S$$

Washing with alcohol gives us a residue of Al and C.

Mg, B, Al, Ce and La in a finely divided state produce the nitride when added to fused KCN. The KCN is first melted in a porcelain crucible at 650° C in the absence of air and poured on a marble slab. It is then remelted in a clay or porcelain crucible and the dry, finely powdered element added in portions. The mixture is stirred from time to time and heated for fifteen minutes after the addition of the last portion. The cooled black mass is placed in warm water for lixiviation. The insoluble nitride and amorphous carbon residue is gently ignited to remove the carbon.

$$2KCN + 3Mg \rightarrow Mg_3N_2 + 2K + 2C$$

Some carbide is liable to be formed also at higher temperatures.

5) Reduction of the Oxide

Wilber (35) in thesis work at the Armour Institute has investigated the preparation of aluminium nitride. Aluminium oxide heated with coke or charcoal in the presence of nitrogen yielded aluminium nitride.

$$Al_2O_3 + 3C + N_2 \rightarrow 2AlN + 3CO$$

He found the best proportions were a bare excess of carbon over the theoretical and 1.0% addition of Fe_2O_3 as a catalyzer. The per cent nitrogen in the finished product was 25.7% N. The reaction is reversible if a large percentage of CO is present. The more impure the gas the higher is the temperature required.

Prof. H. McCormack of the Armour Institute, who directed the above work, gives as the result of his experiment the opinion that the temperature should be from 1775 to 1825° C and the time about 50 minutes. He found that a longer time resulted in a partial

decomposition of the nitride. The greatest trouble in the work was the tendency to surface nitrification to keep the lower part of the charge unchanged. This was best overcome by rotating the tube in which the reaction took place.

6) Electrolysis

Grove (22) and Warren (23) have both succeeded in obtaining zinc nitride by electrolysis. The method consists in electrolyzing a solution of ammonium chloride with a platinum cathode and a zinc anode. The nitride forms around the cathode as a spongy mass or as leafy crystals of the color of graphite. When washed with water and dried by gentle warmth, they were gray and without metallic luster. The specific gravity was 4.6 and they conducted electricity. All the nitrides prepared were brittle and unstable

as regards temperature.

Kramer (24) obtained a shining or spongy mass which he identified as iron nitride by the electrolysis of ammonium chloride and a ferrous salt.

COMMERCIAL PREPARATION

The commercial preparation of the nitrides has been attempted only with the view of utilizing them to produce ammonia or its compounds. there are two general methods for accomplishing this.

The first method consists of exposing the nitride to the action of steam to obtain ammonia direct. This has been chiefly used in the case of Mg, Sn and Pb nitride. Beck (37) has perfected the nitride-steam methods and claims a high efficiency. His nitrides were prepared by bubbling N through an electrolytic cell in which the metals were set free. NaF and KF (melting point 702°C) were used to flux the MgO in some cases. CaF_2 and MgF_2 (Melting point 945° C) were also used. The best results were obtained by fluxing MgO with BaF_2 and CaMgF at 790°. He also cites many other combinations of metals as giving good results.

Borckins and Beck (36) have patented an

electrolytic cell where two suitable metals are set free from the crude salts, alloyed and converted to nitride by means of a stream of N passing over the molten cathode.

The Badische, Analin-und Soda-Fabrik (35) has worked out a method whereby they treat the crude nitride with a limited quantity of acid or alkali so as to obtain an insoluble salt of the metal and a soluble ammonia salt. They have found that the addition of some valuable salt as NaCl facilitates the extraction. For example:

$$2AlN + H_2SO_4 + 6H_2O \rightarrow 2Al(OH)_3 + (NH_4)_2SO_4$$

The nitrides they used were formed by heating the oxides of the metal with coal in the presence of nitrogen. They found that low-grade oxide worked as well as the chemically pure product. Among the oxides used were those of Si, Ti, Zr, Mo, V, Bi, Ce, U, Cr and Al. Sand was given preference on account of its cheapness. They found

that the oxides could be replaced by other oxygen compounds such as silicates, titerates, vanadates, etc.

Many patents have been taken out on the commercial preparation of AlN and for their further discussion the reader is referred to the current literature of the last few years.

EXPERIMENTAL WORK

THE ZINC DUST PROCESS

The Problem

After a careful survey of the literature on the preparation of zinc nitride, it was decided to concentrate all our time on the method consisting of passing N or NH_3 over zinc dust. This was chosen because a preponderance of the evidence showed it to be the most satisfactory so far. As far as commercial preparation of the nitride is concerned, it probably would be the only possible one.

Beyond the fact that when N or NH_3 was passed over zinc at a red heat zinc nitride was obtained, the authors could find no details as to conditions of the reaction. The literature ascribed the highest yields of zinc nitride to cases where the zinc was present as zinc dust and where NH_3 was used. The yields where N was used were not given. The cause of poor yields of nitride was

claimed by one investigator to be due to the establishment of an equilibrium and by another to the reducing action of hydrogen from the ammonia decomposed at the high temperature.

Among the large numbers of variables involved we decided to find the optimum conditions of initial temperature, time, temperature of run, method of cooling, choice between N and NH_3 and preparation of the zinc dust. We realized that zinc had a greater affinity for O than for N especially in such a fine state of subdivision and that the zinc dust contained a large amount of zinc oxide. On this account the preparation of the zinc dust was considered the most difficult of the unknown and, therefore, made the dominant variable.

Outline of the Synthesis

It was decided that for the best results we should purify the gases used by absorbing all moisture, carbon dioxide and oxygen. The absorbent train consisted of bottles filled with 1), an alkaline solution of pynogallic acid, 2), glass wool, 3), sticks of NaOH, 4), soda lime. It was found that the pyrogallic solution lost its efficacy very soon and required frequent renewal. To remedy this, a tube containing Cu gauze which could be heated was placed before the pyrogallic solution in the absorbent train for the nitrogen. An absorbent bottle containing a roll of Cu gauze immersed in a solution of NH_4OH and NH_4Cl was given first place in absorbent train for the ammonia. These auxiliary absorbents for oxygen were inserted after the runs of Series C and greatly prolonged the life of the pyrogallic solution. All joints in the apparatus were sealed with

paraffin.

The second unit of the system was an electric furnace holding the combination tube which was fitted with a pyrometer. It was possible to maintain any temperature from 300° C to 1500° C for a period of 30 minutes with a maximum variation of only 10° C.

The gas was finally passed through a safety bottle and then through water to absorb any free ammonia. The complete set-up is shown in Plates 3 and 4.

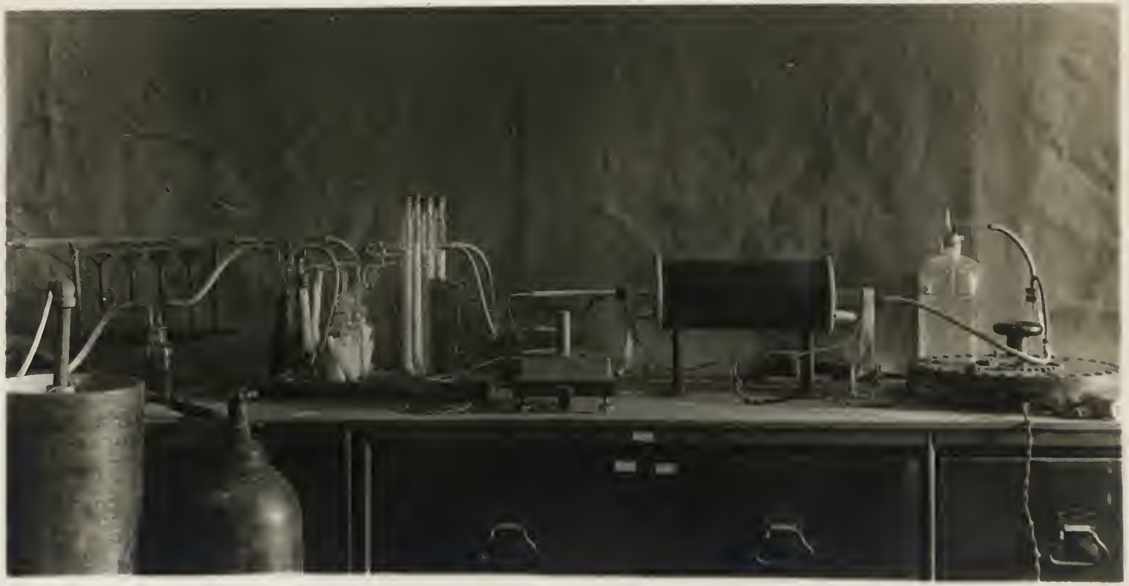

PLATE - 3.

Series A To eliminate or at least materially reduce the amount of oxygen entering the system, we decided to dissolve out the ZnO present in the zinc dust. The dust was exposed to the action of a warm solution of approximately 10% NH_4OH and 20% NH_4Cl for several hours and kept well stirred. It was then filtered on a plain funnel, washed with water, alcohol and ether and dried in vacuo. The pump and desiccator used are shown as No. 1 - Plate 5.

The vacuum was always broken by the admission of N to the desiccator and the boats were loaded in this atmosphere. They were then placed directly into the furnace without exposure to the atmosphere and the run started.

It was thought that the presence of some N along with the NH_3 might tend to shift any equilibrium which might be formed and several runs were made with a mixture

SERIES A

No.	Gas.	Time.	Temp.	How Cooled	$\%Zn_3N_2$
1.	NH_3	30 min.	600°C	In furnace to 20°C	14.4
2.	"	"	"	In air to 20°C	2.01
3.	"	"	"	In furnace to 300°C	12.2
4.	"	"	"	In furnace to 20°C	8.82
5.	N	"	"	In furnace to 250°C	1.63
6.	"	"	"	In air to 20°C	0
7.	"	"	700	In furnace to 250°C	2.02
8.	"	"	400	In furnace to 250°C	1.20
9.	NH_3	"	600	In furnace to 20°C	12.80
10.	N NH_3	"	"	In the air to 20°C	1.20
11.	"	"	"	In furnace to 250°C	6.40
12.	NH_3	"	700	In furnace to 250°C	13.76
13.	N	"	"	In furnace to 20°C	2.32
14.	NH_3	"	500	In furnace to 20°C	9.60

of N and NH_3. Fourteen runs were made under varying conditions.

Series B It was noticed on careful examination of the zinc dust prepared for the latter runs of Series A that some zinc hydroxide was formed during the washing with water.

As this would yield oxide on heating, the washing with water was discontinued and only alcohol and ether were used. The solution of NH_4OH and NH_4Cl was used as before. With the idea of shortening its exposure to the air, the dust was filtered on a Buechner funnel with vacuum. A new lot was prepared for each run and the vacuum desiccator was discarded - the dust damp with ether being introduced directly into the furnace without delay. Five runs were made under various conditions.

SERIES B

No.	Gas.	Time	Temp.	How Cooled	%Zn_3N_2
1.	NH_3	30 mins.	600°	In furnace to 250°C	9.6
2.	"	"	"	" " 20°C	10.4
3.	N	"	"	In furnace to 250°C	1.04
4.	NH_3	"	"	In the air to 20°C	6.04
5.	"	"	"	In furnace to 20°C	28.46

Series C Under the conditions of preparation of Series B, the dust was practically dry and very compact. On more careful consideration it was evident that some air was drawn through the dust during the vacuum filtration. It was also more desirable to have the zinc dust in a less compact state to allow more surface for the gas to attack.

The vacuum filtration was, therefore, given up and the zinc dust was placed in the furnace fairly wet. A new lot was made up for each run. In all runs the furnace was filled with the same gas that was to be used during the run. The amount of ether present lowered the furnace temperature to such an extent that the initial temperature was made 50° higher than that of the run. Several runs were made in which the initial temperature was 20° C and one where it was 300° C. The furnace was then heated up to

SERIES C

No.	Gas	Time	Temp.	How Cooled	%Zn_3N_2
1.	NH_3	30 mins.	600°C	In furnace to 20°	13.2
2.	N	"	"	" 20°	1.2
3.	NH3	"	"	In furnace to 20° (Initial Temp.20°)	.8
4.	"	"	"	"	0
5.	"	"	"	"	.4
6.	"	"	"	In furnace to 20°C (Initial Temp.300°C)	1.61
7.	N	"	"	In furnace to 20°C (Initial Temp. 20°C)	0
8.	"	"	"	"	0

600° C and held there for 30 minutes. Eight runs were made.

Series D The poor results of the last series convinced us that the zinc dust must be practically dry before being heated. The results obtained where the dust was put into the furnace at 20° and heated up to 600° showed that sufficient oxygen was present in the gases to form a protective film of oxide. It was imperative then to introduce the zinc dust into the furnace in such a condition and under such circumstances that the conversion to nitride would begin at once.

It was decided to wash with NH_4OH and NH_4Cl, alcohol and ether as before. The dust was then placed in a vacuum desiccator and dried. Nitrogen was admitted whenever the vacuum was broken. The mass was finely pulverized with a spatula while a current of N was sent through the desiccator and

SERIES D

No.	Gas	Time	Temp.	How Cooled	%Zn_3N_2
1.	NH_3	30 mins.	600°C	In furnace to 20°	17.6
2.	"	"	550	"	17.0
3.	"	"	650	"	17.45
4.	N	"	600	"	9.20
5.	NH_3	"	"	"	29.92
6.	N	"	"	"	12.2
7.	NH_3	"	"	In the air to 20°	9.76
8.	"	15 mins.	"	"	7.2
9.	"	60 "	"	In furnace to 20°	30.95
10.	"	30	"	"	30.88
11.	"	"	700	"	15.6
12.	"	"	550	"	28.0
13.	"	"	400	"	3.2

thoroughly dried before any runs were made. The boats were loaded in an atmosphere of N and placed directly in the furnace at the temperature of the run. Thirteen runs were made.

Series E Under commercial conditions it might be impossible to purify the zinc dust as in the other series. It was therefore thought to be of interest to know the possible yields without any preparation.

The crude zinc dust, of the same grade as used in the other experiments was placed in boats and placed directly in the furnace at the temperature of the run. Five runs were made.

Series F In this series the zinc dust was prepared in the same manner as

SERIES E

No.	Gas	Time	Temp.	How Cooled	%Zn_3N_2
1.	NH_3	15 mins.	500°C	In the air to 20°	1.6
2.	"	"	550	"	2.4
3.	"	30 mins.	600	In furnace to 20°	14.1
4.	"	"	"	In the air to 20°	6.4
5.	N	"	"	In furnace to 20°	5.2

in Series D. The charge was placed in the furnace at 400° C in an atmosphere of NH_3. The nitrogen was immediately displaced by a strong current of H and the furnace held at 400° C for 30 mins. The H was now displaced by NH_3 and the temperature raised to 600° where it was held for 30 mins. The boats were allowed to cool to room temperature in the furnace in an atmosphere of ammonia. The H was obtained from a Kipp generator and filtered through H_2SO_4, glass wool and soda lime.

The analysis of the product showed it to have a content of 35.8% nitrogen.

Apparatus and Materials

The apparatus and materials used in all the experimental work was the best obtainable.

The zinc used was the regular C. P. stick zinc. The zinc dust was procured from Baker and Co. and analyzed 86.7% zinc. The nitrogen was supplied by The Linde Co. and guaranteed to be 99.6% N. The anhydrous ammonia was obtained from Armour and Co. The absorbent solutions used were made up from C.P. salts.

A Hoskins Combination Furnace was used and the temperature could be regulated by means of a dial form of resistance rheostat.

The pyrometer equipment consisted of a Pt - Pt-Rh Thermo-couple made by P. Sieberd, Nan, Germany. The multi-volt meter was made by Siemens and Halske-Berlin and the outfit had been standardized by the Reichs

Austalt, Berlin, Germany. The thermo couple was mounted in a porcelain sheath.

The boats for the charge were composed of Zirconium oxide and the combustion tube was Pyrex glass of 23 mm. diameter.

Methods of Analysis

Nitrogen. A .2000 g. sample was treated with 20 cc. H_2SO_4 (Sp. g. 1.84) and 10 g. of $KHSO_4$ and heated over a bare flame for 30 mins. The solution should now be colorless or just faintly yellow and show no undecomposed particles. The solution is now made up to 200 cc. with distilled water and cooled. A piece of litmus is now added and the solution neutralized in the cold with a concentrated solution of NaOH. Its volume should now be about 350 cc. The Kjeldahl flask is placed on the still and heated till the volume of the liquid is reduced one third. The distillate is absorbed by 25 cc. of N/10 HCl in an Erlenmeyer flask. This solution is titrated with N/10 NaOH and the percentage of N is calculated. At the end of each distillation the last few drops of distillate are tested with litmus as a check. If samples are run contimuously it is unnecessary to

wash the still between each determination.

Farnler (33) has proven conclusively that iron nitrides and many others react quantitatively to give $(NH_4)_2SO_4$ when treated with H_2SO_4. There is therefore little doubt that the reaction with zinc is quantitative.

$$Zn_3N_2 + 4H_2SO_4 \longrightarrow (NH_4)_2SO_4 + 3ZnSO_4$$

Zinc Weight out a .2500 g. sample and dissolve in 10 cc. of concentrated HCl and 10 cc. of water. When solution is complete, dilute to 200 cc. with water, add a strip of litmus and just neutralize with ammonia. Add 3 cc. of conc. HCl and heat to 90° C. Titrate with K_4FeCN_6 using uranium nitrate as an outside indicator. A brown tinge marks the end point.

The standard solution is made by dissolving 22 g. of K_4FeCN_6 in a liter of water and standardizing with ZnO which has been ignited and cooled in a desiccator.

Metallic Zinc in the presence of Zinc Oxide

Put a 1.000 g. sample into a 600 cc. Erlenmeyer flask with 50 g. of ferric alum (large crystals) and 100 cc. of water. The whole must be constantly stirred by a suitable motion of the flask. Large crystals do not all dissolve but aid in the agitation. As soon as the sample is all dissolved add 100 cc. of H_2SO_4 (1 : 10) and titrate against N/10 $KMnO_4$.

THE CYANIDE PROCESS

During a period through which our millivoltmeter was being repaired it was decided to try to obtain zinc nitride from the decomposition of the cyanide.

A. C. Vournas (16) claims that zinc cyanide can be partially oxidized in the presence of N by NH_4NO_3 to zinc nitride.

$$3Zn(CN)_2+12NH_4NO_3 \rightarrow Zn_3N_2+14N+6CO_2+24H_2O$$

The apparatus used consisted of a tall beaker fitted with a cork having provision for a thermometer, an inlet tube of N and a space for the escape of the gases. This beaker was supported in an oil bath for the purpose of careful heating. The inlet tube for N extended well to the bottom of the beaker. The apparatus is shown as No. 3 in Plate 4.

The $Zn(CN)_2$ used in the experiments was secured by its precipitation from a solution of $ZnCl_2$ with KCN. The precipitate was

filtered, washed free of chlorides and dried at 105° C.

Several runs were made using the exact stoichiometrical amounts of reagents e.g., 1 part of $Zn(CN)_2$ to 2.72 parts of NH_4NO_3. Various slight excesses of NH_4NO_3 were also tried but seemed to have no effect and to decompose explosively at the close of the reaction. The rate of heating did not influence the reaction. The N was supplied at a fairly rapid rate.

The various changes with temperature were not sharp but were about as follows:- Mixture starts to liquify at 120°C, a thin paste at 180° C, a clear yellow liquid at 240° C at which the evolution gas starts. There is an even evolution of white fumes and steam till the last few minutes of the reaction when brown fumes appear. The end of the reaction is always marked by a slight puff or a fairly violent explosion when much

excess NH_4NO_3 is present.

In all runs the product was light yellow powder which on analysis gave zero N content and proved to be wholly zinc oxide.

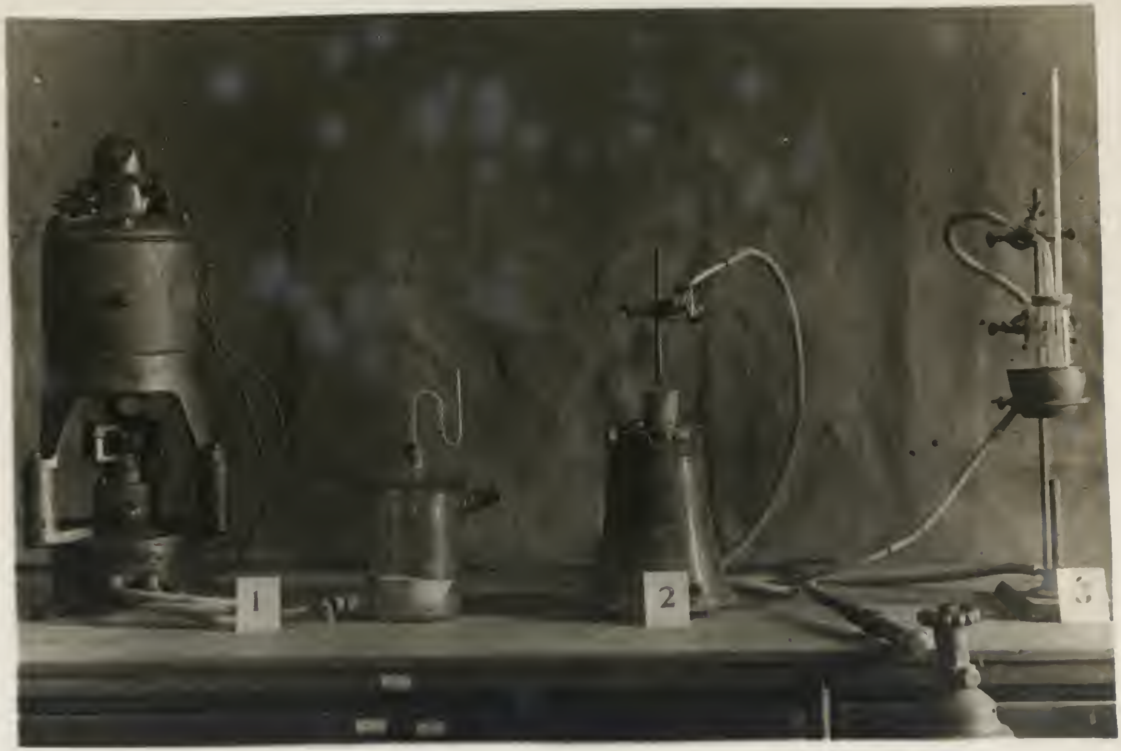

PLATE-4.

THE ALLOY EXPERIMENTS

By combining all the high yield samples of the nitride, we obtained quite an amount of powder which on analysis gave 20.4% zinc nitride. This was used in the alloy experiments. The zinc used was C. P. stick zinc.

In the first experiment the zinc nitride was simply poured on the surface of the molten zinc and stirred in. The temperature was about 450° C and all the nitride oxidized. Analysis gave 0% nitrogen.

It was now decided to fold a quantity of Zn_3N_2 into some zinc foil and plunge the capsule below the surface of the molten zinc. This was done and the mass well stirred. Partial oxidation of the nitride was noted. Analysis gave .03% N,

The conditions were the same for the third trial but a current of N was passed over the surface of the molten zinc and the capsule then immersed. Set-up is shown

in No. 2, Plate 4. Barely any oxidation could be detected. The nitride powder used was dark gray and the oxidized powder was dark brown. Analysis gave:-

Sample 3 - .29% N

Sample 4 - .61% N

Sample 5 - .48% N

DISCUSSION

Zinc Dust Process

Throughout all the experiment a deposit of zinc oxide was noted on the walls of the combustion tube. This was white in places and yellow in others. A white vapor was also observed at the start of the reaction and was identified as zinc oxide. Whenever the boats containing the nitride were removed from the furnace at a temperature greater than 200° C the nitride was observed to burn and a white and yellow crust of oxide was formed. In Series F when the H was passed the reduction of the oxide deposited on the walls of the tube was apparent and later on while the NH_3 was passing, the reformation of the oxide could be seen.

It is apparent from these indications that oxygen in the system is the chief obstacle to the preparation of zinc nitride. It can also be seen from the experiment with H that

the method of preparation finally used (Series D) gives us a zinc dust free from oxide and that the oxygen is present as a gas. It is probable that an increase in the number of absorbtion bottles for oxygen and the passage as H along with the NH_3 would solve the difficulty and give almost theoretical conversion.

The zinc dust prepared under Series D showed great activity. It combined instantly with water to form the hydroxide. On exposure to the air it oxidized vigorously. On one occasion it was noted that the oxidation of about 50 g. of the dust was sufficient to raise the temperature of the mass to 120° C in about 6 mins.

In cases where the nitride had become oxidized the color varied from white or yellow to a deep brown. The darker shades indicated quite complete oxidation with some admixture of metal while the white

or yellow was pure ZnO. The nitride varied in color from a light gray to a dark gray or black in the higher yields.

Comparisons In all cases comparisons are made under such conditions that there remains but the one variable.

PREPARATION

Conditions of comparison. - NH_3 passed for 30 mins. at 600° and product cooled in furnace to 20°.

A - 1	14.4%	Zn_3N_2	D - 5	29.92%	ZN_3N_2
B - 2	10.4	"	E - 3	14.10	"
C - 1	13.2	"	F -	35.80	"

Choice of a Gas

Conditions of comparison - heating for 30 mins. at 600° and cooling in furnace to 250°.

A - 3	NH_3	12.20%	Zn_3N_2
A- 5	N	1.63%	"
A - 11	N NH_3	6.40%	"

Initial Temperature

Conditions of comparison - heating in NH_3 for 30 mins. at 600° and cooling in furnace to 20° C.

C - 1	Same as Run	13.20%	Zn_3N_2
C - 4	20° C	0.0%	"
C - 6	300° C	1.61%	"

Temperature of Run

Conditions of comparison - heating for 30 mins. in NH_3 and cooling in the furnace to 20° C.

D - 10	600°	30.88%	Zn_3N_2
D - 11	700	15.60%	"
D - 12	550	28.00%	"
D - 13	400	3.20%	"

Time

Conditions of comparison - heating at 600° in NH_3 and cooling in furnace to 20°.

D - 8	15 mins.	7.20%	Zn_3N_2
D - 9	60 mins.	30.95%	"
D - 10	30 mins.	30.88%	"

Method of Cooling

Conditions of comparison - heating in NH_3 for 30 mins. at 600° C.

A - 1	In furnace to 20°	14.4% Zn_3N_2
A - 2	In the air	2.01% "
A - 3	In furnace to 300°	12.20% "
A - 12	In furnace to 250°	13.76% "

From the above it can be seen that the ideal conditions to date for the preparation of zinc nitride are:-

Zinc dust should be well agitated with a warm solution of NH_4OH and NH_4Cl (10% and 20% respectively) for several hours. It should then be filtered without suction and washed with alcohol and ether. The pasty mass is to be immediately placed in a vacuum desiccator and dried. From this on it must always be kept in an atmosphere of N.

The boats should be loaded in an atmosphere of N and placed directly in the furnace at an initial temperature of 600° C. NH_3 should be passed fairly fast through the tube and

the furnace held at 600° C for 30 mins. Further heating has little effect on the product. The nitride must be left to cool in the furnace in NH_3 till the temperature has fallen to at least 200° C.

The Cyanide Process

The reaction given is of a type which one would not ordinarily expect to be fulfilled. However it is quite probable that the proportions indicated are incorrect and that another equation by reducing the amount of NH_4NO_3 used would give the nitride.

The Alloy Experiments

It is unfortunate that the work on the preparation of the nitride took such a large amount of time that only a few trials of the alloy could be made. These were, however, sufficient to show that an alloy of zinc nitride with zinc is possible. A higher percentage of nitrogen would probably be obtained with a purer nitride. For lack of time, no attempt was made to study the properties of the alloy. It is silvery white and in appearance it much resembles zinc itself.

ZINC AS A METAL

PHYSICAL PROPERTIES OF ZINC

Zinc is a bluish white metal possessing a bright metallic luster and is capable of taking a high polish.

Pure zinc is appreciably hardened by quenching in water after casting. The pure metal is malleable and may be rolled into thin sheets at the ordinary temperature, but commercial cast zinc is moderately hard and brittle at the ordinary temperature, a flat ingot, or cake, of the metal being fairly easily broken across under a blow from a heavy hammer. Although commercial zinc is very much less brittle than antimony or bismuth the crystalline structure of the metal causes it to split and break up if hammered or rolled cold. The fracture exhibits large crystal faces of high metallic luster, especially when the metal is free from iron. The appearance of the fracture is characteristic and affords an indication

of the purity of the metal. The fracture is more largely crystalline the higher the temperature of casting is above the melting point of the metal. When bent the cast metal emits a sound resembling the "cry of tin" but somewhat more feeble.

The commercial metal becomes malleable and ductile if heated to a temperature from 100° C to 150° C after which treatment it retains its malleability when cold sufficiently to admit of being rolled into thin sheet or drawn into wire. On a large scale, however, the metal is rolled hot. At a temperature above 205° C zinc again becomes so brittle that it may be pulverized in an iron mortar. In common with other metals, zinc is hardened by mechanical treatment, such as rolling, and requires annealing at a low temperature to restore its malleability.

Measurements of the tensile strength of rolled zinc have been made by H.F. Moore

(38) which show that zinc hardened by rolling is in an unstable condition at the ordinary temperature and undergoes a gradual change to the soft state. Thus the scleroscope hardness of rolled zinc was found to be 36 and after 97 days the hardness had fallen to 31.0.

Zinc is less tenacious than most metals in common use, its tensile strength varying greatly according to the mode of preparation. According to Karmarsch the tensile strength is about 2,800 lbs. per square inch when cast and between 18,700 and 22,200 lbs. per square inch when in sheets or wire. Robert Austen gives its ultimate tensile strength (kind of metal not stated) as 7000 to 8000 lbs. per square inch against 4,600 lbs. for cast tin and 19,000 lbs. for cast copper. According to Wertheim a permanent elongation of .5 mm. per meter of a bar 1 mm. square, took place with tensions of .75, 1.00 and 3.2 kg.

according as to whether the bar was drawn, annealed, or cast; he found also that the yield point of a wire 1 mm. in diameter was 1.5 kg. with cast metal and 12.5 kg. with drawn and annealed. According to Karmarsch the absolute strength of cast zinc is 197.5 kg. per sq. cm. and of sheet and wire 1,315 to 1,560 per sq. cm. Trantwine determined that a prism of cast zinc, 1 inch square and 4 inches high was compressed 1/400 of its height by 2,00 lbs., 1/200 by 4,000 lbs., 1/600 by 6000 lbs., 1/38 by 10,000 lbs. and 1/15 by 20,000 lbs., while under 40,000 lbs. it yielded rapidly and broke into pieces. (39).

The hardness of cast zinc by Brinell is 38.1 compared with copper 40.0 and silver 24.8.

The thermal conductivity of zinc is variable (or has not been determined accurately) ranging from 19 (Wiedemann) to 64.1

(Calvert and Johnson) silver being 100. According to Roberts-Austen the thermal conductivity of zinc is 28.1.

Its electrical conductivity is 16.92, mercury at 0° C being unity. Rating silver at 100, the electrical conductivity of zinc is 24.06 according to Becquerell, 27.39 according to Matthiessen, and 29.90 according to Weiller. The electrical resistance of a wire 1 mm. in diameter and 1 mm. in length is .0724 ohms. According to Roberts-Austen the coefficient of linear expansion of zinc is .00291; according to Figean it is .002905 for 100° C from 0° C upward; according to Calvert and Johnson it is .002193 for hammered zinc; according to the British Board of Trade units it is .002532.

Between 0° and 100° C the specific heat of zinc is .09555 (Regnault); other authorities give it as .0927 from 0° to 100° C and .1015 from 100° to 300° C.

Comparison with other Metals

It can be seen on reference to Plate 5 that zinc compares quite well with the other metals save in tensile strength. Its melting point is conveniently low. In ductility, density and specific heat it compares very well with iron. It is fourth in the list as regards thermal conductivity and third in specific resistance.

Taking all in all the only weak point in zinc is its tensile strength and this as we have pointed out before would probably be remedied by alloying with zinc nitride.

	Melting Point.	Tensile Strength. (Relative)	Ductility. (Relative)	Density.	Coeff. of Linear Expansion.	Sp. Heat.	Thermal Conductivity	Specific Resistance.
Zn	419.°C	2	8	7.1	26.3×10^{6}	.0935	28.1	.0724
Al	657.°	10	7	2.6	25.5 "	.2190	50.4	.0369
Sn	232.°	1	9	7.3	22.3 "	.0562	15.2	.1678
Pb	327.°	1	10	11.4	27.6 "	.0305	8.3	.2437
Cu	1083.°	16	6	8.9	16.7 "	.0936	91.8	.0202
Cast Fe	1530.°	12	5	7.6	10.2 "	.1190	14.4	.1234

PLATE – 5.

SUMMARY

SUMMARY

A thorough search has been made through all the current periodicals and the American, English and German Abstracts for a little over a hundred years back. In most cases the original articles have been consulted. We believe that the section on nitrides and the bibliography represents a thorough survey of the field.

The experimental work on zinc nitride has shown the chief difficulties of the synthesis; and the best conditions and plan of attack have been mapped out.

The experiments have proven that the alloy zinc-zinc nitride is at least possible. It is unfortunate that lack of time prevented a study of its properties. However it is hoped that it will remedy the one fatal defect of zinc - large

crystal structure and lack of tensile strength.

We have found the subject of the utmost interest and hope to continue the work at a future date or see others work along the same line.

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